



# Theoretical Investigation of the Magnetic Exchange Interactions in Copper(II) Oxides under Chemical and Physical Pressures

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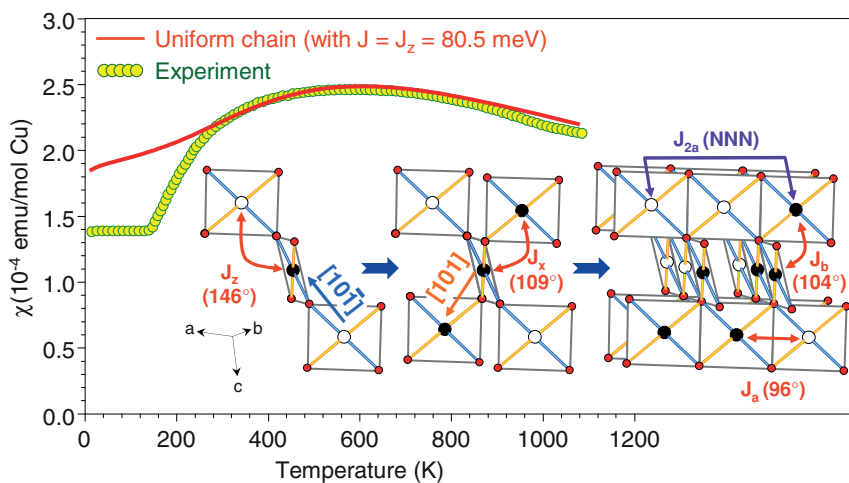
It remains a challenge to understand the unconventional mechanisms that cause high- $T_C$  superconductivity in cuprate superconductors, high- $T_C$  multiferroicity in CuO, or low-dimensional magnetism in the spin-Peierls transition compounds such as CuGeO<sub>3</sub>. A common feature of all these copper oxide compounds (containing Cu<sup>2+</sup> ions) is the presence of large magnetic superexchange interactions  $J$ . It is a general strategy to apply chemical and/or physical pressure in order to tune these exotic properties. Here we show theoretically, for the first time, the impact of physical pressure on  $J$  on CuO, for which we predict a strong enhancement of the low-dimensionality of the magnetic interactions and the spin-frustration at high-pressures. Such modifications are expected to strongly influence the multiferroic properties of CuO. We finally demonstrate that PBE0 hybrid DFT calculations provide reliable  $J$  values for a wide range of copper(II) oxides compounds, i.e. CuGeO<sub>3</sub>, BaCu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, BaCu<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, and La<sub>2</sub>CuO<sub>4</sub>.

The interest for CuO has been revived in 2008 by the discovery by Kimura *et al.* of magnetically induced electric polarization at 230 K<sup>1</sup>. Indeed, CuO exhibits a type-II multiferroic behavior, i.e. the ferroelectric polarization is triggered by a specific magnetic order. Recently, several efforts have been carried out to elucidate the relationship between the magnetic properties and the high-temperature multiferroicity in CuO<sup>2,3</sup>. In particular, one important ingredient explaining the high- $T_C$  value of CuO is the existence of a high Néel temperature ( $T_N = 230$  K), which is due to the presence of large antiferromagnetic superexchange interactions  $J$ . Thus, tuning  $T_C$  towards room-temperature implies to be able to tune the magnetic exchange interactions in CuO. However, the experimental estimation of the  $J$  values is not straightforward and strongly depends on the technique. On the other side, a theoretical estimation of the  $J$  values could be realized by using the Heisenberg spin Hamiltonian. Here, based on PBE0 hybrid density functional calculations, we propose an efficient and reliable evaluation of the impact of physical pressure on  $J$  in CuO. In addition, we also apply these calculations to a series of low-dimensional cuprate compounds, allowing to estimate the impact of the chemical pressure on  $J$ .

## Results

**CuO at ambient pressure and temperature.** CuO is a particularly interesting case because it exhibits at least four superexchange interactions<sup>9,10</sup>, namely  $J_a$ ,  $J_b$ ,  $J_x$ ,  $J_z$ , and three super-superexchange interactions, namely  $J_{2a}$ ,  $J_{2b}$ ,  $J_{2c}$  (Fig. 1). Recently we have shown that  $J_{2a} > J_{2b} \gg J_{2c}$ <sup>11</sup>. In the present study we focus on the global effect of the next nearest neighbour (NNN) interactions, i.e.  $J_2 = J_{2a} + J_{2b} + J_{2c}$ . Such complexity is due to the three-dimensional nature of the atomic structure of CuO<sup>12</sup>. This structure can be seen to consist of corner- and edge-sharing square-planar CuO<sub>4</sub> units, which form (-Cu-O)<sub>∞</sub> zigzag chains running along the [10-1] and [101] directions of the chemical unit cell (Fig. 1).

Before discussing how physical pressure affects the 5 essential  $J$  values of CuO a validation of our method is needed. It was demonstrated that our PBE0<sup>13</sup> hybrid calculations are able to accurately reproduce both  $J$  values and magnetic susceptibility data<sup>14</sup> (Fig. 1). More specifically, the reported experimental  $J$  values<sup>15,16</sup>  $J[10-1] = J_z = 80$  meV and  $J[101] = J_x = 5$  meV, are in excellent agreement with the calculated ones, namely  $J_z = 80.5$  meV and  $J_x = 3$  meV. The magnetic susceptibility modelling has been based, to a first approximation, on a  $S=1/2$  AFM uniform Heisenberg chain model<sup>17</sup> using the  $J_z$  deduced from our PBE0 hybrid calculations, i.e.  $J_z = 80.5$  meV. However, at

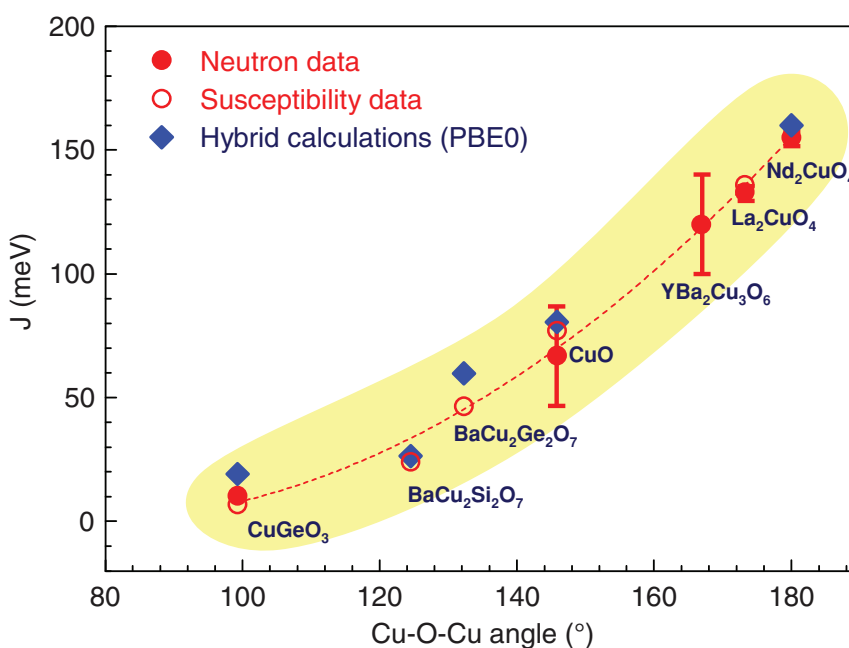


**Figure 1 | Structural and magnetic properties of CuO at ambient pressure.** The experimental magnetic susceptibility<sup>14</sup> is compared to a simulated one based on an  $S = 1/2$  Heisenberg uniform chain model with  $J = J_z = -80.5 \text{ meV}$ . The experimental susceptibility has been corrected by the temperature independent contribution  $\chi_0$ , i.e.  $\chi_{exp}(T) = \chi_{mol}(T) - \chi_0$ , with  $\chi_0 = +20 \times 10^{-6} \text{ emu/mol}$ , as found from the fit of the high-temperature magnetic susceptibility and a  $g$  factor of 2.095 obtained from EPR measurements<sup>24</sup>. A progressive construction of the crystal structure and the magnetic ground state of CuO is shown, indicating the most important ( $J_z$ ) and other (smaller) magnetic exchange couplings ( $J_x$ ,  $J_y$ ,  $J_b$  and  $J_{2a}$ ). At low temperature ( $T < T_L$ ), the CuO magnetic structure consists of FM and AFM arrangements along the  $[101]$  and  $[10\bar{1}]$  crystallographic directions. The oxygen atoms are represented by small red circles, and the  $\text{Cu}^{2+}$  sites are depicted as filled and empty circles, representing up-spin and down-spin, respectively.

low temperature ( $T < 260 \text{ K}$ ), the 1D uniform chain model overestimates the magnetic susceptibility of CuO. This result indicates an onset of 2D spin correlations<sup>18</sup>, which can be used to roughly estimate the interchain couplings, i.e.  $J_{inter} \approx 260 \text{ K} \approx 22 \text{ meV}$ . Indeed, the second largest  $J$  value in our calculations is  $J_2 = 19.6 \text{ meV}$ , which couples the  $(-\text{Cu}-\text{O})_\infty$  zigzag chains, defined by the intrachain term  $J_z$ .

**Effect of chemical pressure on  $J$  in low-dimensional cuprates.** For over half a century, the Goodenough-Kanamori-Anderson rule<sup>4,6</sup> is routinely used to qualitatively explain the relation between  $J$  and the atomic arrangement of the magnetic centers in a given system. For instance, in copper oxide compounds, the nearest-neighbor (NN) Cu-Cu spin interaction  $J$  is expected to change from antiferromagnetic (AFM) to ferromagnetic (FM) when the angle  $\phi$  of the

Cu-O-Cu bond goes from  $180^\circ$  to  $90^\circ$ . Recently Shimizu *et al.* have proposed such a correlation between  $J$  and the Cu-O-Cu bond angle  $\phi$  in low-dimensional cuprates<sup>7,8</sup>, based on neutron and Raman scattering, and susceptibility measurements. By tuning the chemical composition, i.e. the chemical pressure, copper oxide compounds give access to the full range of Cu-O-Cu bond angles from  $90^\circ$  to  $180^\circ$ . Figure 2 shows how the magnetic exchange coupling in a series of copper oxide compounds depends on the Cu-O-Cu bond angle. For this study we considered the spin-Peierls transition compound  $\text{CuGeO}_3$ , the quasi-one-dimensional AFM compounds  $\text{BaCu}_2\text{Si}_2\text{O}_7$  and  $\text{BaCu}_2\text{Ge}_2\text{O}_7$ , and the 2D AFM cuprate  $\text{La}_2\text{CuO}_4$ , which under doping becomes an high- $T_C$  superconductor. For simplicity the small buckling of the Cu-O-Cu bonds in the  $\text{CuO}_2$  sheets in  $\text{La}_2\text{CuO}_4$  has been neglected in the present PBE0 hybrid calculations



**Figure 2 | Principal superexchange interaction  $J_z$  as a function of the Cu-O-Cu bond angle  $\phi$  for various low-dimensional cuprates.** Our calculations are compared to experimental data taken from neutron and Raman scattering, and susceptibility measurements<sup>7</sup>.



(i.e. a Cu-O-Cu bond angle of  $180^\circ$  is assumed), as in  $\text{Nd}_2\text{CuO}_4$ . The agreement between available experimental data<sup>7</sup> and these calculations is very good and validates that the PBE0 hybrid functional is well-suited to estimate the magnetic exchange parameters in all these copper(II) oxide compounds.

**Effect of physical pressure on  $J$  in CuO.** An alternative to probe the correlation between  $J$  and the Cu-O-Cu bond angle  $\phi$  in cuprates would be physical pressure applied to a specific compound. However, to our knowledge, no experimental and/or theoretical investigations of the physical pressure dependence of  $J$  have been reported so far. In Fig. 3 we show the calculated pressure and temperature dependence of the  $J$  values in CuO. For this purpose, we have considered the atomic structures that were refined at different temperatures<sup>19</sup> and pressures<sup>20</sup>. The new  $J$  values for each temperature and pressure have been deduced using the same strategy as reported in ref. 9. By increasing pressure or decreasing temperature, CuO undergoes a volume contraction, leading to significant modifications in the Cu-O-Cu bond angles. The present calculations show how these structural rearrangements affect the  $J$  values of CuO. For instance, the intrachain  $J_z$  value undergoes a reduction of 8% when the temperature is raised up to  $T = 999$  K, but an increase of 46% when the pressure is increased up to 8.8 GPa. Thus  $J_z$  can be tuned from 74 to 117 meV by varying these two variables,  $T$  and  $P$ . The interchain coupling  $J_2$ , however, is nearly insensitive to both pressure and temperature. As a consequence, the ratio  $J_z/J_2$  increases from 3.6 to 5.3 when pressure is increased from 0.1 GPa to 8.8 GPa. Similar effects of  $P$  and  $T$  are observed for the smaller  $J$  parameters, namely  $J_a$ ,  $J_b$  and  $J_x$ . As pressure is increased the FM couplings are enhanced, and an additional FM coupling appears, i.e.  $J_a$ .

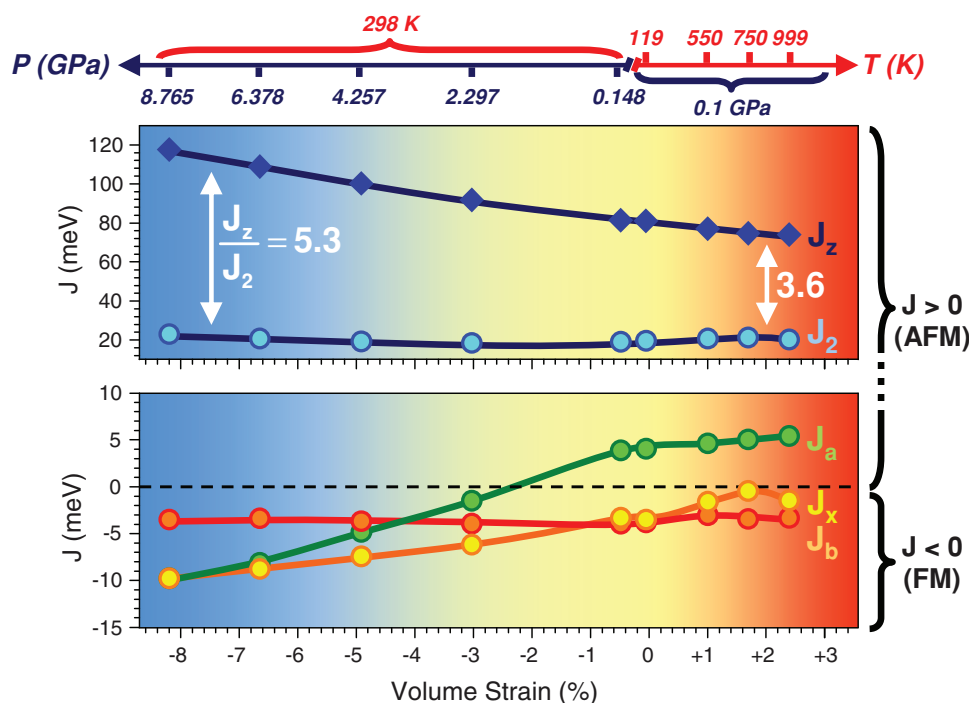
It should be noted that  $J_a$  and  $J_2$  correspond to the NN and NNN interactions in the chains based on edge-sharing  $\text{CuO}_4$  plaquettes (Fig. 1). Under high-pressure, the NN coupling  $J_a$  becomes FM, while the NNN  $J_2$  coupling remains AFM, with a ratio  $J_2(\text{NNN}) \approx -2 J_a(\text{NN})$ , i.e. the spin frustration is increased by a factor of two

compared to ambient conditions. Consequently, the present calculations show that applying high-pressure on CuO will induce: (i) an increase of the larger AFM coupling ( $J_z$ ) implying an increase of the Néel temperature ( $T_N$ ) with pressure, (ii) a larger stability of the incommensurate phase, directly related to the increase of 1D magnetic character and spin frustration in CuO. Our results are consistent with recent neutron diffraction experiments<sup>21,22</sup>, revealing that  $T_N$  increases slightly from 230 K (ambient pressure) to 235 K ( $P = 1.8$  GPa), and the stability range of the incommensurate spiral magnetic phase is increased, with a lock-in temperature  $T_L$  decreasing from 213 K (ambient pressure) to 207 K ( $P = 1.8$  GPa).

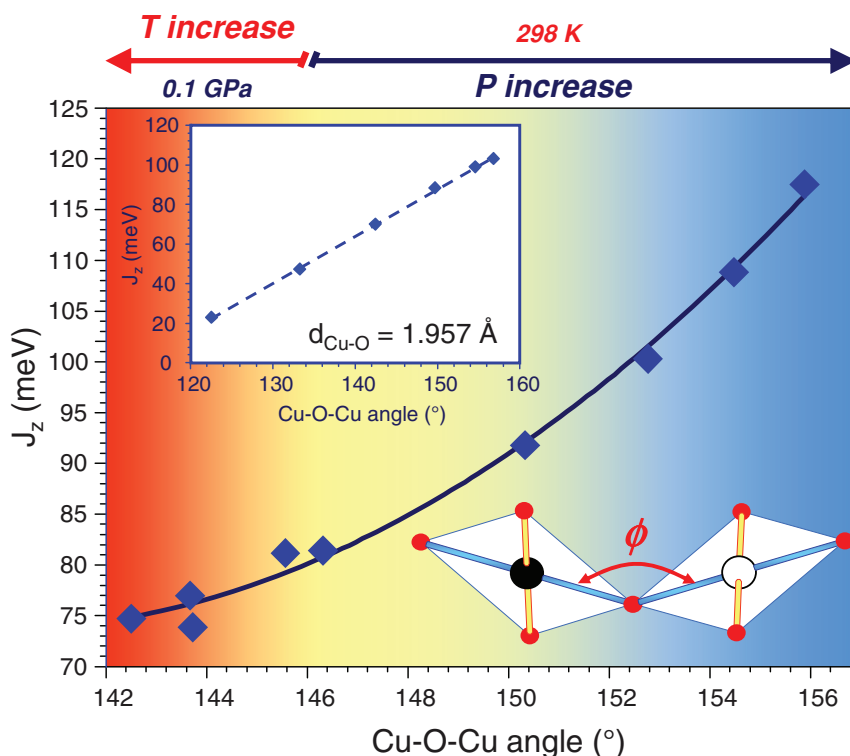
The large increase of  $J_z$  under high pressure emerges mainly from an increase of the Cu-O-Cu bond angle from  $143.7^\circ$  (at  $T = 999$  K and  $P = 0.1$  GPa) to  $155.9^\circ$  (at  $T = 298$  K and  $P = 8.8$  GPa), as evidenced in Fig. 4. This non-linear correlation between  $J$  and  $\phi$  is very similar to the one previously proposed by Shimizu *et al.*<sup>7</sup> (see also Fig. 2). However, in their case the angle variation is a consequence of chemical pressure whereas in our case it is physical pressure. In this context it is of interest that previous works<sup>7,8</sup> found no correlation between the Cu-O bond length and  $J$ . In order to analyze the effects on the magnetic exchange interactions, namely the contribution from the bond length and bond angle, we have generated artificial CuO atomic structures, under positive and negative pressure but keeping the Cu-O distances constant inside the  $\text{CuO}_4$  plaquette ( $d_{\text{Cu-O}} = 1.957$  Å), i.e. the volume change induces only bond angle variations (Fig. 3 inset). In this hypothetical situation, the correlation between  $J_z$  and  $\phi$  becomes linear over the whole angle range from  $120^\circ$  to  $160^\circ$ . This shows that the influence of the bond length variation on  $J$  is smaller than the bond angle variation, but is significant, leading to the non-linear correlation between  $J$  and  $\phi$ . The analogy shown here between physical and chemical pressures is very pronounced.

## Discussion

In the present work, we demonstrate that an efficient and reliable estimation of the magnetic exchange parameters of a wide variety of



**Figure 3 | Pressure and temperature dependence of the magnetic exchange couplings of CuO.** In this figure,  $P$  and  $T$  are increasing to the left and to the right, respectively. The volume strain of CuO is given by the volume variation divided by the initial volume (at ambient pressure and temperature). By convention positive and negative  $J$  values represent AFM and FM interactions, respectively.



**Figure 4** | Principal superexchange interaction  $J_z$  as a function of the Cu-O-Cu bond angle  $\phi$  for CuO under high-temperature and high-pressure. In this figure, P and T are increasing to the right and to the left, respectively. The inset shows the evolution of  $J_z$  in CuO as a function of the Cu-O-Cu bond angle  $\phi$  for CuO under positive and negative pressure, while keeping constant the Cu-O bond length in the CuO<sub>4</sub> plaquettes ( $d_{\text{Cu-O}} = 1.957 \text{ \AA}$ ).

copper oxide compounds is achievable by using the PBE0 hybrid functional. Moreover, the present theoretical investigation shows that by applying 8.8 GPa to CuO, an increase of 46% of the largest  $J$  value is expected, implying that the Néel temperature will be also enhanced under pressure, paving the way for the first room-temperature multiferroic material.

## Methods

DFT calculations were performed using the WIEN2k program package<sup>23</sup> with the PBE0<sup>13</sup> hybrid functional. For each temperature and pressure, the magnetic exchange couplings of CuO have been evaluated considering nine ordered spin states depicted in ref. 9, and assuming collinear arrangements of the magnetic moments. A similar strategy has been applied to the six hypothetical CuO structures in which the Cu-O bond length were kept constant (for positive and negative pressure – see inset of Fig. 3). The magnetic exchange couplings of CuGeO<sub>3</sub>, BaCu<sub>2</sub>M<sub>2</sub>O<sub>7</sub> (with M = Si, Ge) and La<sub>2</sub>CuO<sub>4</sub> have been evaluated using magnetic unit cells consisting of 4, 4 and 2 formulae units, respectively.

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### Author contributions

X.R. designed and performed the calculations, and drafted the manuscript. X.R., K.S. and P.B. analysed and discussed the results.

### Additional information

**Competing financial interests:** The authors declare no competing financial interests.

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